

## Functional Methacryloyloxy Acetals: V.\* Electrophilic Addition of Carboxylic Acids to 2-Vinyloxyethyl Methacrylate

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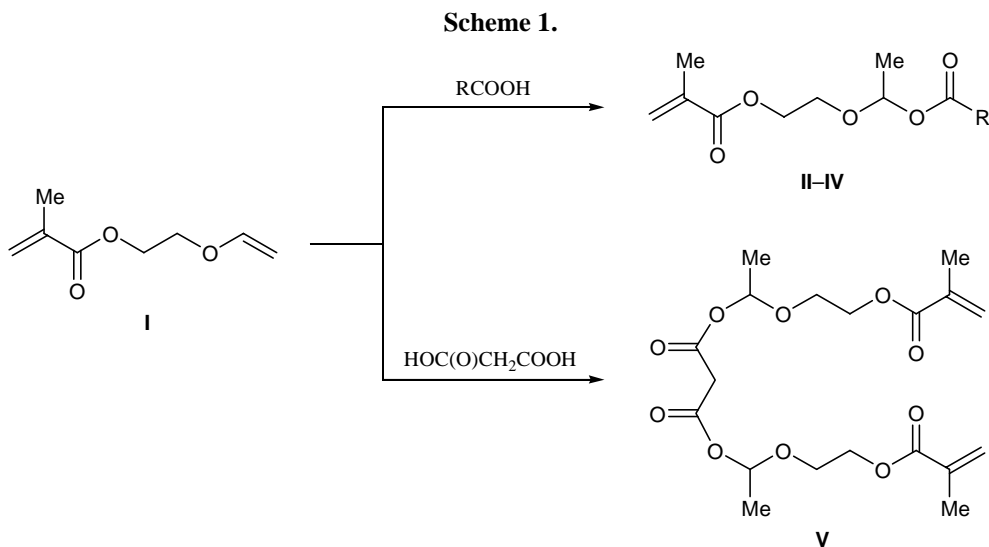
**Abstract**—Mono- and dicarboxylic acids (acetic, methacrylic, *E*-crotonic, and malonic) quantitatively add to 2-vinyloxyethyl methacrylate under mild conditions (1 wt %  $\text{CF}_3\text{COOH}$ , 20–60°C, 1–4 h) according to the Markownikoff rule to give the corresponding mono- and bis-adducts with high regio- and chemoselectivity. The products may be regarded as a new family of functionalized methacrylates.

The chemistry of accessible vinyloxyalkyl methacrylates [2–5] has been extensively studied in the recent years [1, 6–12]. These compounds readily take up alcohols [6], polyols [7], and triazoles [1] at the vinyloxy group, which acts as an “anchor” function, to give new polyfunctional methacryloyloxy acetals as promising monomers, comonomers, cross-linking agents, building blocks, and starting materials for the synthesis of biologically active substances.

With the goal of extending the synthetic potential of vinyloxyalkyl methacrylates, as well as of obtaining new information on electrophilic addition to the

vinyloxy group therein, in the present work we examined reactions of 2-vinyloxyethyl methacrylate with carboxylic and dicarboxylic acids. The synthesis of materials for new technologies, based on selective addition of various reagents, including carboxylic acids, to the vinyloxy group of functionally substituted vinyl ethers with retention of the active functionalities (such as epoxy ring, triple bond, halogen atom, etc.) has developed successfully during the last decades [2, 13–20].

Our experiments showed that carboxylic acids, both monobasic (including unsaturated ones) and dibasic,



\* For communication IV, see [1].

**Table 1.** Refractive indices and elemental analyses of compounds **II–V**

Comp. no.	$n_D^{20}$	Found, %		Formula	Calculated, %	
		C	H		C	H
<b>II</b>	1.4324	54.78	6.93	C <sub>10</sub> H <sub>16</sub> O <sub>5</sub>	55.54	7.45
<b>III</b>	1.4352	59.11	7.03	C <sub>12</sub> H <sub>18</sub> O <sub>5</sub>	59.49	7.48
<b>IV</b>	1.4496	58.86	8.07	C <sub>12</sub> H <sub>18</sub> O <sub>5</sub>	59.49	7.48
<b>V</b>	1.4542	54.77	7.07	C <sub>19</sub> H <sub>28</sub> O <sub>10</sub>	54.80	6.78

namely acetic, methacrylic, *E*-crotonic, and malonic, add to the vinyloxy group of 2-vinyloxyethyl methacrylate (**I**) in the presence of a catalytic amount of trifluoroacetic acid. The reaction is regio- and chemoselective, and the corresponding Markownikoff mono- (**II–IV**) and bis-adducts (**V**) are formed in almost quantitative yield (Scheme 1). Compounds **II–V** constitute a new family of functionalized methacrylates, acrylatomethacrylates, and bis-methacrylates.

The reaction takes 4 h at room temperature or 1 h on heating to 50–60°C. The addition of (*E*)-crotonic acid and malonic acid to vinyl ether **I** was carried out in 1,2-dimethoxyethane which favored homogeneous reaction conditions. Using acetic and methacrylic acids as examples, we have found that the addition does not occur in the absence of trifluoroacetic acid even on prolonged heating to 70–80°C. These findings indicate that the vinyloxy group in vinyloxyalkyl methacrylates is less reactive with respect to electrophiles than the same group in alkyl vinyl ethers. The latter take up carboxylic acids in the absence of a catalyst at room temperature or on heating [13, 21, 22].

The progress of reactions was monitored by the disappearance from the IR spectrum of the reaction mixture of absorption bands belonging to hydroxy (3375 cm<sup>-1</sup>) and vinyloxy groups (830–850, 963–965, 1205, 1367, 1620, and 3060 cm<sup>-1</sup>) group, as well as by the appearance of a characteristic broadened absorption band at 1010–1200 cm<sup>-1</sup> due to O–C–O stretching vibrations in the acetal fragment. Here, the bands at 1640 and 1720 cm<sup>-1</sup> (C=C–C=O) and 3100 cm<sup>-1</sup> (CH<sub>2</sub>=) corresponding to the methacryloyloxy group (which is not involved in the reaction) are retained. In the <sup>1</sup>H NMR spectra of the reaction mixtures, we observed a doublet from the methyl proton ( $\delta$  1.39–1.45 ppm) and a quartet from the CH proton ( $\delta$  5.94–6.02 ppm; <sup>3</sup>*J* = 5.2 Hz), which are typical of the acetal (acylal) moiety.

Compounds **II–V** are weakly colored liquids, which are readily soluble in most organic solvents. If the reactions are performed with freshly distilled reactants, the products require no additional purification. Their structure is consistent with the IR and <sup>1</sup>H NMR spectra and elemental composition (Tables 1, 2). It should be emphasized that compounds **II–V** do not undergo disproportionation typical of unsymmetrical methacryloyloxy acetals [6]. On the other hand, adducts **III–V** having two unsaturated groups undergo polymerization at 200–250°C (during vacuum distillation) even in the presence of radical inhibitors (such as hydroquinone and *N*-phenyl- $\beta$ -naphthylamine).

We also made an attempt to effect the reaction of 2-vinyloxyethyl methacrylate (**I**) with accessible dibenzylphosphinic acid which is readily obtained in the synthesis of (*E*)-olefins from tribenzylphosphine oxide and aldehydes [23]. However, the reactants did not change over a period of 1 h at 20–60°C in 1,2-dimethoxyethane in the presence of a catalytic amount of CF<sub>3</sub>COOH; under more severe conditions (85°C, 9 h), polymerization of vinyl ether **I** at the vinyloxy group occurred. In the IR spectrum of the polymeric product (which was isolated after separation of unreacted dibenzylphosphinic acid from the reaction mixture), the intensity of absorption bands belonging to the vinyloxy group (830–850, 963–965, 1205, 1367, 1620, and 3060 cm<sup>-1</sup>) relative to that of the C–O vibration bands was appreciably lower than in the initial 2-vinyloxyethyl methacrylate (**I**).

Thus we have developed a new simple procedure for the synthesis of reactive monomers and cross-linking agents having a chemically labile acetal–acylal functionality. Our results support the general character of the approach to functionalized acrylates via selective addition of various reagents at the “anchor” vinyloxy group in vinyloxyalkyl methacrylates [1, 6–12].

## EXPERIMENTAL

The IR spectra were recorded on a Bruker IFS-25 spectrometer from samples prepared as thin films. The <sup>1</sup>H NMR spectra were measured on a Bruker DPX-400 instrument (400 MHz) using CDCl<sub>3</sub> as solvent and HMDS as internal reference. The initial mono- and dicarboxylic acids were commercial products which were purified by known methods (by distillation or recrystallization); their physical properties were consistent with published data. 2-Vinyloxyethyl methacrylate (**I**) was synthesized and purified by the procedures described in [2–4].

**Table 2.** IR and <sup>1</sup>H NMR spectral parameters of compounds **II–V**

Comp. no.	IR spectrum, $\nu$ , $\text{cm}^{-1}$	<sup>1</sup> H NMR spectrum ( $\text{CDCl}_3$ ), $\delta$ , ppm ( $J$ , Hz)						
		OCHO, q ( $^3J$ )	Me, d ( $^3J$ )	=CH <sub>2</sub> ( $^2J$ , $^4J$ )	MeC=, br.s	CH <sub>2</sub> OC(O), m	CH <sub>2</sub> , m	R
<b>II</b>	515, 558, 609, 656, 815, 839, 864, 933, 961, 1012, 1040, 1092, 1143, 1167, 1243, 1298, 1320, 1373, 1453, 1638, 1721, 1739, 2889, 2957, 2995, 3106	5.94 (5.2)	1.39 (5.2)	5.56 d.q ( <i>trans</i> , 1.5, 1.6), 6.11 br.s ( <i>cis</i> )	1.93	4.27	3.79, 3.87 (1H each)	2.05 s (3H, Me)
<b>III</b>	539, 591, 652, 814, 845, 945, 1010, 1036, 1091, 1126, 1161, 1262, 1296, 1318, 1358, 1378, 1391, 1452, 1639, 1718, 2888, 2925, 2952, 2988, 3107	6.02 (5.2)	1.45 (5.2)	5.57 d.q ( <i>trans</i> , 1.5, 1.6), 6.12 br.s ( <i>cis</i> )	1.95	4.30	3.82, 3.91 (1H each)	1.94 s (3H, Me), 5.60 s (1H, =CH <sub>2</sub> , <i>trans</i> ), 6.15 s (1H, =CH <sub>2</sub> , <i>cis</i> )
<b>IV</b>	513, 655, 690, 745, 815, 844, 919, 945, 968, 991, 1040, 1099, 1140, 1166, 1193, 1268, 1297, 1319, 1346, 1356, 1380, 1390, 1447, 1639, 1656, 1719, 2885, 2943, 2994, 3052, 3106	6.02 (5.2)	1.40 (5.2)	5.56 d.q ( <i>trans</i> , 1.5, 1.6), 6.11 br.s ( <i>cis</i> )	1.93	4.25	3.77, 3.87 (1H each)	1.88 d (3H, Me, $^3J = 7.0$ ), 5.84 d.d (1H, CH=, $^3J = 15.5$ , $^3J = 1.6$ ), 7.01 m (1H, =CHMe)
<b>V</b>	516, 603, 655, 818, 833, 946, 1035, 1089, 1141, 1166, 1298, 1321, 1362, 1391, 1405, 1454, 1638, 1720, 1751, 2890, 2956, 2994, 3107	6.01 (5.16)	1.42 (5.16)	5.58 d.q ( <i>trans</i> , 1.5, 1.6), 6.12 br.s ( <i>cis</i> )	1.94	4.22	3.80, 3.93 (2H)	3.40 s (2H, CH <sub>2</sub> )

**Addition of acetic acid to 2-vinyloxyethyl methacrylate.** Trifluoroacetic acid, 0.02 g (1 wt %), was added to a mixture of 1.56 g (0.01 mol) of vinyl ether **I** and 0.60 g (0.01 mol) of acetic acid, and the mixture was stirred for 1 h at 60°C until absorption bands of vinyl ether **I** disappeared completely from the IR spectrum of the mixture. The product was distilled under reduced pressure (88°C, 2 mm) in the presence of hydroquinone (1 wt %). Yield of 2-[1-(acetoxo)-ethoxy]ethyl methacrylate (**II**) 2.05 g (95%).

Adduct **III** was synthesized in a similar way but without vacuum distillation. Yield 2.37 g (98%).

**Addition of (*E*)-crotonic acid to 2-vinyloxyethyl methacrylate.** Vinyl ether **I**, 1.56 g (0.01 mol), and trifluoroacetic acid, 0.02 g (1 wt %), were added to a solution of 0.86 g (0.01 mol) of (*E*)-crotonic acid in 2 ml of 1,2-dimethoxyethane. The mixture was stirred for 1 h at 60°C until absorption bands of vinyl ether **I** disappeared completely from the IR spectrum of the

mixture. The solvent was removed under reduced pressure to isolate 2.38 g (98%) of 1-[2-(methacryloyloxy)-ethoxy]ethyl (*E*)-2-butenate (**IV**).

Likewise, from 0.52 g (0.005 mol) of malonic acid in 2 ml of 1,2-dimethoxyethane and 1.56 g (0.01 mol) of vinyl ether **I** in the presence of 0.02 g (1 wt %) of trifluoroacetic acid, we obtained 2.03 g (98%) of bis-adduct **V**.

The refractive indices, elemental analyses, and spectral parameters of compounds **II–V** are given in Tables 1 and 2.

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